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Considering a single spur, let n_e be the number of radicals which escape recombination as a result of hydrogen produced in that spur. Then an increment of dose, dR, to the system will cause radicals within the spur to disappear as a result of hydrogen produced in other spurs; so

$$-dR/d\log n = R_0 n_e/n, \tag{14}$$

where R_0 is the initial value of $dR/d\log n$. Assuming that a particular spur is affected only by the hydrogen produced after its formation the integration of (14) between the pertinent limits gives

$$n_0 = n_e R_0/(R_0+R_T-R), \tag{15}$$

R_T-R being the dose received after the formation of the spur. We now want $\bar{n}_0$, an average value for all the spurs produced throughout the whole radiation interval. Since dR/R_T is the fraction of the total number of spurs produced in the increment dR our desired average is

$$\bar{n}_0/n_e = (R_0/R_T)\int_0^{RT} [dR/(R_0+R_T-R)] \tag{16}$$
$$= (R_0/R_T)\log[1+(R_T/R_0)].$$

An estimate of $\bar{n}_0/n_e$ which is independent of Eq. (16) is not possible at this time, though it seems that it should certainly be greater than the ratio of N_0 to the number of free radicals formed when radiation is done in the presence of iodine. This ratio (for 16 J/g radiation) is $5.65\times10^{17}/2.0\times10^{18}=0.28$. The most plausible results from Eq. (16) are obtained by assuming $\bar{n}_0/n_e=0.70$ for the 16 J/g treatment. This requires values of 0.39 and 0.145 for the 64 and 256 J/g treatments.

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Energy Moment Method Applied to Nuclear Quadrupole Splitting of Nuclear Magnetic Resonance Lines

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Expressions giving the sum of the energy values, raised to the second and third power, for a nucleus interacting with a static magnetic field and a static electric field gradient are derived. Several applications of this method for obtaining the values of the components of the electric field gradient tensor from observed NMR spectra are suggested.

1. INTRODUCTION

THE method usually applied in extracting the values of the components of the electric field gradient tensor V_{ij} at the site of a nucleus in a single crystal from experimental magnetic resonance data proceeds as follows: The values of the transition frequencies ν, determined as functions of the angles specifying the direction of the magnetic field with respect to some set of reference axes fixed in the crystal, are compared with certain theoretical expressions for the ν's containing V_{ij} as parameters. These expressions are approximate only, being derived by perturbation calculations. The state of the art has recently been reviewed by Cohen and Reif.[1]

There is, however, another method, known as the method of energy moments, which has the advantage of being exact. This method has been discussed by Brown and Parker[2,3] in connection with the problem considered here. Their final results are only stated in the system of principal axes of V_{ij}, and this system is very often unknown in advance. It is the purpose of this note to give a short derivation of formulas pertaining to the general situation.

2. THEORY

The Hamiltonian for the system is (in frequency units)[1]

$$\mathcal{H} = -\nu_0 I_p n_p + \tfrac{1}{6}\alpha V_{ij} T_{ij}, \tag{1}$$

where

$$\alpha = 3eQ/2I(2I-1)h, \tag{2}$$

and

$$T_{ij} = \tfrac{3}{2}(I_i I_j + I_j I_i) - \delta_{ij} I_s I_s \tag{3}$$

(summation over dummy indices implied).

Here ν_0 is the unperturbed nuclear Larmor frequency in the applied magnetic field H_0. The direction of H_0 is specified by the components n_p of a unit vector in an *arbitrary system* of rectangular axes of reference fixed in the crystal. I_p and V_{ij} are the components of the spin vector operator and of the electric field gradient tensor, respectively, in this coordinate system. Finally,

[1] M. H. Cohen and F. Reif, Solid State Phys. **5**, 321–438, (1957).
[2] L. C. Brown and P. M. Parker, Phys. Rev. **100**, 1764 (1955).
[3] P. M. Parker and L. C. Brown, Am. J. Phys. **27**, 509 (1959).

Q is the quadrupole moment of the nucleus, and I is its spin quantum number.

It is well known, that in these experiments only the traceless part of V_{ij} may be determined. It is, therefore, as a matter of convenience customary to assume for V_{ij} in (1) that

$$V_{ii}=0. \tag{4}$$

We also note that

$$V_{ij}=V_{ji}. \tag{5}$$

We shall now calculate the diagonal sum of the Hamiltonian operator raised to some integral power. We shall write

$$S_n=\mathrm{Tr}\{\mathcal{H}^n\}. \tag{6}$$

The general form of S_n may be constructed by using the following two principles:

(a) Only terms with ν_0 raised to an even power will appear (corresponding to the fact that experimentally one can not discriminate between a given direction of the magnetic field and the opposite direction).

(b) As $\mathcal{H}^n$ is a scalar operator, S_n will be a "c-number" scalar, i.e., only scalar invariants formed by combination of the tensor V_{ij} and the vector n_i can appear in the expression for S_n.

Let us find the general form of S_3: According to (a), (1), and (6), only terms of the form $\nu_0^2\alpha$ and α^3 can appear. The coefficient to $\nu_0^2\alpha$ must, due to (b), (1), and (6), be a linear combination of those scalars, which can be constructed by using the vector n_i twice and the tensor V_{ij} once. There is only one such scalar in the present situation, namely,

$$n_iV_{ij}n_j.$$

[The other possibility $n_in_iV_{jj}$ gives zero on account of (4).] Analogously the coefficient to the term α^3 contains the scalars which can be constructed by using the tensor V_{ij} three times, the only possibility being

$$V_{ij}V_{js}V_{si}.$$

[The determinant of a symmetric, traceless second-order tensor is proportional to the expression just given and a scalar like $V_{ij}V_{ji}V_{ss}$ is zero on account of (4).]

Thus S_3 must be of the form

$$S_3=6g_2(I)\nu_0^2\alpha n_iV_{ij}n_j+\tfrac{4}{3}g_3(I)\alpha^3V_{ij}V_{js}V_{si}, \tag{7}$$

where g_2 and g_3 are functions, yet to be determined, of the spin quantum number I. The choice of specific values for the numerical factors in (7) is made for convenience.

In the same way (and utilizing $n_in_i=1$), it is easily shown that S_2 must be of the form

$$S_2=g_1(I)\nu_0^2+\tfrac{2}{3}g_4(I)\alpha^2V_{ij}V_{ji}. \tag{8}$$

For S_1 we have

$$S_1=0. \tag{9}$$

To determine the functions $g_1\cdots g_4$ we make a specific choice for V_{ij} and n_i. Putting $n_1=n_2=0$, $n_3=1$ and $V_{11}=V_{22}=-1$, $V_{33}=2$ together with $V_{ij}=0$ for $i\neq j$ (thus $V_{ij}V_{ji}=6$, $V_{ij}V_{js}V_{si}=6$, and $n_iV_{ij}n_j=2$) gives, according to (1):

$$\mathcal{H}=-\nu_0I_3+\tfrac{1}{3}\alpha[3I_3^2-(I_1^2+I_2^2+I_3^2)].$$

In a representation where the operators I_3 and $I_1^2+I_2^2+I_3^2$ are both diagonal, S_2 and S_3 are then easily calculated, and by comparison with (7) and (8), we obtain

$$\begin{aligned} g_1(I)&=\tfrac{1}{3}I(I+1)(2I+1),\\ g_2(I)=g_4(I)&=\tfrac{1}{60}(2I-1)g_1(I)(2I+3),\\ g_3(I)&=\tfrac{1}{42}(2I-3)g_2(I)(2I+5); \end{aligned} \tag{10}$$

(7) and (8), when written in the system of principal axes of V_{ij} are of course identical to the results of Parker and Brown.[2]

Higher moments may be calculated along the same lines as indicated above with a few more complications, but as discussed below a knowledge of S_2 and S_3 will normally be enough for the determination of V_{ij}.

3. APPLICATIONS

We shall consider the usual experimental setup, where the crystal can be rotated about, say, the X axis, which is perpendicular to the direction of the magnetic field H_0. The angle between H_0 and the Y axis is denoted by θ_x (measured positive counterclockwise looking down the X axis), so that the unit vector $\bar{n}$ is given by $(0, \cos\theta_x, -\sin\theta_x)$. Equations (7) and (8) then take the form

$$S_2=g_1(I)\nu_0^2+g_2(I)\nu_Q^2(1+\tfrac{1}{3}\eta^2), \tag{8a}$$

$$\begin{aligned} S_3=3g_2(I)\nu_0^2\nu_Q[&\phi_{yy}+\phi_{zz}+(\phi_{yy}-\phi_{zz})\\ &\times\cos2\theta_x-2\phi_{yz}\sin2\theta_x]+g_3(I)\nu_Q^3(1-\eta^2). \end{aligned} \tag{7a}$$

Here

$$\nu_Q=[3/2I(2I-1)](e^2Qq/h),$$

and

$$\phi_{ij}=(1/eq)V_{ij},$$

where eq and η have their usual meaning.[1]

The dimensionless tensor ϕ_{ij} satisfies the following conditions:

$$\phi_{ii}=0, \tag{11}$$

$$\phi_{ij}\phi_{ji}=\tfrac{3}{2}(1+\tfrac{1}{3}\eta^2), \tag{12}$$

$$\phi_{ij}\phi_{js}\phi_{si}=\tfrac{3}{4}(1-\eta^2), \tag{13a}$$

or equivalently

$$\|\phi_{ij}\|=\tfrac{1}{4}(1-\eta^2). \tag{13b}$$

In the following discussion, because of $g_3(\frac{3}{2})=0$ we limit ourselves to the case $I\neq\frac{3}{2}$. Further it is assumed that the last terms in (7a) and (8a) are not negligible with respect to the first terms in these

equations. This assumption means that (in the language of the usual methods) second-order shifts are observable. It should, however, be stressed that the present method requires that the full spectrum must be observable, in order to be able to construct the energy level scheme and from this calculate S_2 and S_3.

(a) If one principal axis of ϕ_{ij} is known in advance we choose this as the X axis (giving $\phi_{xy}=\phi_{xz}=0$) and obtain from the rotation pattern about this axes [*vide* (8a) and (7a)] the values of:

$$\nu_Q(\phi_{yy}-\phi_{zz}),$$

$$\nu_Q\phi_{yz},$$

$$3g_2(I)\nu_0^2\nu_Q(\phi_{yy}+\phi_{zz})+4g_3(I)\nu_Q^3\,||\,\phi_{ij}\,||,$$

and

$$\nu_Q^2\phi_{ij}\phi_{ji}.$$

This gives four equations for the three unknown quantities $\nu_Q\phi_{yy}$, $\nu_Q\phi_{zz}$, and $\nu_Q\phi_{yz}$ (we have $\phi_{xx}=-\phi_{yy}-\phi_{zz}$). It is readily seen that this determines these quantities uniquely (and that a certain overdetermination exists, giving a check on the experimental data). Thus knowing in full the tensor $\nu_Q\phi_{ij}$, the location of the principal axes in the Y–Z plane as well as ν_Q and η are then found by standard methods.

(b) If nothing is known in advance about ϕ_{ij}, we shall indicate two methods to obtain first ν_Q and η.

(1) If three spectra, with the magnetic field in the X, Y and Z direction, respectively, are measured we see from (7a) and (11) that

$$S_3(\theta_x=0)+S_3(\theta_y=0)+S_3(\theta_z=0)=3g_3(I)\nu_Q^3(1-\eta^2).$$

From this and the value of $\nu_Q^2(1+\frac{1}{3}\eta^2)$ [from (8a)], ν_Q and η may be obtained separately. Note that this result is correct for an arbitrary choice of three mutually perpendicular axes.

(2) If S_3 is observed for two different values of the magnetic field (the crystal being arbitrary but fixed in orientation) we get from (7a) (in an obvious notation)

$$(\nu_0''/\nu_0')^2S_3'-S_3''=[(\nu_0''/\nu_0')^2-1]g_3(I)\nu_Q^3(1-\eta^2),$$

giving the value of $\nu_Q^3(1-\eta^2)$, which combined with the value of $\nu_Q^2(1+\frac{1}{3}\eta^2)$ from (8a) gives ν_Q and η.

Knowing ν_Q and η, a rotation diagram about the X axis will now, according to (7a) and (11) give ϕ_{yy}, ϕ_{zz}, $\phi_{xx}=-\phi_{yy}-\phi_{zz}$ and ϕ_{yz}. Substituting these values in (12) and (13b) gives two equations connecting the still unknown components ϕ_{xy} and ϕ_{xz}. In a ϕ_{xy}–ϕ_{xz} plane these equations describe a circle and an ellipse, both centered in (0, 0). Of the four possible pair of values for (ϕ_{xy}, ϕ_{xz}) a unique pair may be selected by the results of a single measurement with the magnetic field in the X–Y or X–Z plane. In practice a complete rotation pattern about the Y axis (say) may be preferred, giving quite an overdetermination of the problem.

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Proton Magnetic Resonance Spectrum of HDO† *

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The proton magnetic resonance spectrum of the distinct species HDO has been observed in dilute solutions of H_2O and D_2O in carefully purified organic solvents. The HDO triplet is centered 0.030±0.003 ppm upfield from the H_2O resonance. The proton–deuteron spin–spin coupling constant A_{HD} is 1.1±0.1 cps. Approximate theories which provide explanations for the coupling constant and chemical shift are discussed.

RESULTS

THE proton magnetic resonance spectrum of HDO has not been observed previously, primarily because the rapid exchange of protons and deuterons in H_2O–D_2O mixtures effectively averages the small differences in magnetic environment for protons in H_2O and HDO. However, the exchange rate can be slowed down considerably if the H_2O–D_2O mixture is diluted with a solvent of low basicity which has been carefully purified. At sufficiently high dilution, then, one might expect to observe the spectrum of the mixed isotopic species HDO. Figure 1(b) is the proton resonance spectrum in the water region of an acetone solution containing equimolar amounts of H_2O and D_2O at a total concentration of 1.1 mole/liter. This unsymmetrical multiplet is a superposition of the spectra of the

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